

MENU**SEARCH****INDEX****DETAIL****JAPANESE**

1 / 1

PATENT ABSTRACTS OF JAPAN

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(54) ALIGNING AGENT FOR LIQUID CRYSTAL AND METHOD OF MANUFACTURING LIQUID CRYSTAL ALIGNMENT FILM

(57)Abstract:

PROBLEM TO BE SOLVED: To provide an aligning agent for a liquid crystal which has little irregularity in the film thickness during printing and to provide a liquid crystal alignment film having no irregular thickness.

SOLUTION: The aligning agent for a liquid crystal for printing and coating contains γ -butyrolactone and N-methyl-2-pyrrolidone as the solvent for a polyamic acid and/or soluble polyimide as the reaction product of a tetracarboxylic acid dianhydride and a diamine. The liquid crystal alignment film is manufactured by using the aforementioned agent.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[The technical field to which invention belongs] This invention relates to the manufacture approach of a liquid crystal orientation agent and the liquid crystal orientation film. It is related with the approach of manufacturing the liquid crystal orientation film, from a liquid crystal orientation agent with the good spreading nature at the time of printing, and this still more detailed liquid crystal orientation agent.

[0002]

[Description of the Prior Art] It is made sandwich structure with the substrate with a transparent electrode which has the liquid crystal orientation film which consists of polyimide etc. conventionally the nematic mold liquid crystal which has a forward dielectric anisotropy, and TN as the major axis of a liquid crystal molecule comes to be twisted between substrates continuously 90 to 270 degrees, and the liquid crystal display component (TN, STN mold display device) which has a STN mold liquid crystal cell are known. The orientation of the liquid crystal in this TN and a STN mold liquid crystal display component is formed with the liquid crystal orientation film with which rubbing processing was performed. Although this liquid crystal orientation film is applied using print processes, when the thickness nonuniformity at the time of printing is large and there is specifically variation **50A or more as thickness, there is a problem of affecting a display property and an electrical property.

[0003]

[Problem(s) to be Solved by the Invention] The purpose of this invention is to offer the liquid crystal orientation agent of a new presentation. Other purposes of this invention are to solve said conventional trouble and offer the small liquid crystal orientation agent of the thickness nonuniformity at the time of printing. The purpose of further others of this invention is to offer the approach of manufacturing the liquid crystal orientation film using the above-mentioned liquid crystal orientation agent of this invention. The purpose and advantage of further others of this invention will become clear from the following explanation.

[0004]

[Means for Solving the Problem] the mixed solvent which according to this invention the above-mentioned purpose and advantage of this invention contain at least one sort of polymers chosen as the 1st from the polyamic acid and fusibility polyimide which are (A) tetracarboxylic dianhydride and the resultant of diamine and (B) gamma-butyrolactone, and a N-methyl-2-pyrrolidone, and is in the range whose content of a N-methyl-2-pyrrolidone is 0.1 - 50 % of the weight -- since -- it is attained by the liquid crystal orientation agent for printing spreading characterized by becoming. Moreover, according to this invention, the above-mentioned purpose and advantage of this invention are attained by the manufacture approach of the liquid crystal orientation film characterized by applying the above-mentioned liquid crystal orientation agent of this invention to a substrate by printing, and heating [2nd], and forming a paint film.

[0005] The liquid crystal orientation agent of this invention consists of a specific polymer (A) and a specific mixed solvent (B). The polyamic acid of a polymer (A) is obtained by making tetracarboxylic

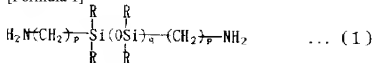
dianhydride and diamine react in a solvent. As this tetracarboxylic dianhydride, for example Butane tetracarboxylic dianhydride, 1, 2, 3, 4-cyclobutane tetracarboxylic dianhydride, 1, 2 and 3, 4-cyclopentane tetracarboxylic dianhydride, 2, 3, 5-TORIKARUBOKI gardenia fruit clo pentyl acetic-acid 2 anhydride, 3 and 5, 6-TORIKARUBOKISHI norbornane-2-acetic-acid 2 anhydride, 2, 3, 4, 5-tetrahydrofuran tetracarboxylic dianhydride, 1, 3, 3a, 4 and 5, 9b-hexahydro-5-tetrahydro - 2, the 5-dioxo-3-furanyl-[1 and 2-naphth c]-furan -1, 3-dione, The 5-(2, 5-dioxo tetrahydro FURARU)-3-methyl-3-cyclohexene -1, 2-dicarboxylic acid 2 anhydride, Aliphatic series, such as the bicyclo [2, 2, 2]-oct-7-en -2, 3 and 5, and 6-tetracarboxylic dianhydride, and alicycle group tetracarboxylic dianhydride; Pyromellitic acid 2 anhydride, - benzophenone tetracarboxylic dianhydride, 3, 3', and 3, 3', 4, and 4', 4'-biphenyl sulfone tetracarboxylic dianhydride, 1, 4, 5, 8-naphthalene tetracarboxylic dianhydride, 2, 3 and 6, 7-naphthalene tetracarboxylic dianhydride, 3, 3', 4, 4'-biphenyl ether tetracarboxylic dianhydride, 3, 3', 4, 4'-dimethyl diphenyl silane tetracarboxylic dianhydride, 3,3',4,4'-tetraphenylsilane carboxylate dianhydride, 1, 2, 3, 4-furans tetracarboxylic dianhydride, 4, and 4'-bis(3, 4-dicarboxy phenoxy) diphenyl sulfide 2 anhydride, 4 and 4'-bis(3, 4-dicarboxy phenoxy) diphenylsulfone 2 anhydride, 4 and 4'-bis(3, 4-dicarboxy phenoxy) diphenyl propane 2 anhydride, 3, 3', 4, 4'-perfluoro isopropylidene phthalic acid dianhydride, 3, 3', 4, 4'-biphenyl tetracarboxylic dianhydride, bis(phthalic acid) phenyl phosphine oxide 2 anhydride, p-phenylene-bis(triphenyl phthalic acid) 2 anhydride, m-phenylene-bis(triphenyl phthalic acid) 2 anhydride, a screw (triphenyl phthalic acid) -4 and 4' - diphenyl ether 2 anhydride, a screw (triphenyl phthalic acid) -4, and 4' -- aromatic series tetracarboxylic dianhydride, such as - diphenylmethane 2 anhydride, can be mentioned.

[0006] Among these, butane tetracarboxylic dianhydride, 1, 2 and 3, 4-cyclobutane tetracarboxylic dianhydride, 2, 3, 5-TORIKARUBOKI gardenia fruit clo pentyl acetic-acid 2 anhydride, the 5-(2, 5-dioxo tetrahydro FURARU)-3-methyl-3-cyclohexene -1, 2-dicarboxylic acid 2 anhydride, 1, 3a [3], 4, 5, and 9b-hexahydro-5-tetrahydro - 2, the 5-dioxo-3-furanyl-[1 and 2-naphth c]-furan -1, and 3-dione are desirable.

[0007] As a diamine compound, for example Moreover, p-phenylene diamine, m-phenylenediamine, -diamino diphenylmethane, and 4 and 4', 4'-diamino bibenzyl, - diamino diphenyl sulfide, and 4 and 4', 4'-diaminodiphenyl sulfone, 4 and 4'-diamino diphenyl ether, 1, 5-diamino naphthalene, The 3 and 3-dimethyl -4, a - diamino biphenyl, and 4', 4'-diamino biphenyl, A - diamino diphenyl ether, and 4', 3'-diamino benzophenone, [3, and] 3, a - diamino benzophenone, and 4', 4'-diamino benzophenone, A 2 and 2-bis[4-(4-amino phenoxy) phenyl] propane, 2 and 2-bis[4-(4-amino phenoxy) phenyl] hexafluoropropane, A 2 and 2-bis(4-aminophenyl) hexafluoropropane, 2, and 2-bis[4-(4-amino phenoxy) phenyl] sulfone, 1, 4-bis(4-amino phenoxy) benzene, 1, 3-bis(4-amino phenoxy) benzene, A 1, 3-bis(3-amino phenoxy) benzene, 9, and 9-bis(4-aminophenyl)-10-hydronalium anthracene, 9 and 9-bis(4-aminophenyl) fluorene, 4, and 4'-methylenebis (2-chloroaniline), 2, 2', 5, and 5' - tetra-chloro -4 and 4' - diamino biphenyl -- 2, 2'-dichloro -4, the 4'-diamino -5, a 5'-dimethoxy biphenyl, Aromatic series diamine which has hetero atoms, such as aromatic series diamine; diamino tetraphenylthiophenes, such as 3, 3'-dimethoxy -4, and a 4'-diamino biphenyl; 1 and 1-meta-xylylene diamine, 1,3-propanediamine, a tetramethylenediamine, pentamethylene diamine, A hexamethylenediamine, heptamethylene diamine, octamethylene diamine, Nonamethylene diamine, 1, 4-diamino cyclohexane, isophorone diamine, Tetrahydro dicyclopentadienylenediamine, hexahydro -4, 7-methano INDANIREN dimethylene diamine, Aliphatic series or alicycle group diamines, such as tricyclo [6, 2, 1, 02.7]-undecylene dimethyldiamine, 4, and 4'-methylenebis (cyclohexylamine); the following type (1)

[0008]

[Formula 1]



[0009] (the inside of a formula, and R -- the hydrocarbon group of carbon numbers 1-12 like aryl

groups, such as cycloalkyl radicals, such as chain-like alkyl groups, such as a methyl group, an ethyl group, and a propyl group, and a cyclohexyl radical, or a phenyl group, -- being shown -- p -- 1-3q -- each of 1-20 -- an integer is shown)

[0010] The diamino ORGANO siloxane expressed with **** is mentioned. - diamino diphenylmethane, and p-phenylene diamine [among these], 4, and 4' 4, 4' bis[- diamino diphenyl ether, 2, and 2-] [4-(4-amino phenoxy) phenyl] propane, 9, and 9-bis(4-aminophenyl) fluorene 2 and 2-bis[4-(4-amino phenoxy) phenyl] hexafluoropropane, 2, and 2-bis(4-aminophenyl) hexafluoropropane is desirable. These are independent or can be used combining two or more sorts. Moreover, these diamines may use a commercial item as it is, or they may use it, re-returning.

[0011] If the polyamic acid generated at a reaction may be dissolved as the above-mentioned organic solvent used for a reaction, there will be especially no limit. For example, gamma-butyrolactone and a N-methyl-2-pyrrolidone are used preferably. As for the amount of the organic solvent used, it is desirable to make it the total amount of tetracarboxylic dianhydride and all diamine compounds become 0.1 - 30% of the weight to the whole quantity of a reaction solution. Moreover, 0-150 degrees C of reaction temperature in this case are more preferably performed with the reaction temperature of 0-100 degrees C.

[0012] The operating rate of tetracarboxylic dianhydride and a diamine compound is 0.3-1.2Eq preferably [making the acid-anhydride radical of tetracarboxylic dianhydride into 0.2-2Eq to 1Eq of amino groups in a diamine compound], and more preferably.

[0013] The fusibility polyimide used for this invention is obtained by heating the above-mentioned polyamic acid or imide-izing it under existence of a dehydrating agent and an imide-ized catalyst. 60-200 degrees C of reaction temperature in the case of imide-izing with heating are 100-170 degrees C more preferably. When reaction temperature tends to be in advance of a reaction at less than 60 degrees C and 200 degrees C is exceeded, the molecular weight of fusibility polyimide may fall greatly. Moreover, the reaction in the case of imide-izing under existence of a dehydrating agent and an imide-ized catalyst can be performed in the above mentioned organic solvent. Reaction temperature is 60-150 degrees C more preferably 0-180 degrees C of usual states. As a dehydrating agent, acid anhydrides, such as an acetic anhydride, a propionic anhydride, and anhydrous trifluoroacetic acid, can be used. Moreover, as an imide-ized catalyst, although tertiary amine, such as a pyridine, a collidine, a lutidine, and triethylamine, can be used, for example, it is not limited to these. As for the amount of the dehydrating agent used, it is desirable to consider as 1.6-20 mols to one mol of repeat units of polyamic acid. Moreover, as for the amount of the imide-ized catalyst used, it is desirable to consider as 0.5-10 mols to one mol of dehydrating agents to be used.

[0014] Thus, intrinsic-viscosity [eta_{inh}] of the polyamic acid obtained and fusibility polyimide (measurement) is 0.05 - 5 dl/g more preferably 0.05 to 10 dl/g about intrinsic viscosity on the following said conditions among ln etare/C and C=0.5 g/dl, 30 degrees C, and a N-methyl-2-pyrrolidone.)

[0015] In addition, it can use together to extent to which the polymer which generates the alcohols which are poor solvents, ketones, ester, ether, halogenated hydrocarbon, and hydrocarbons does not deposit in said organic solvent as a reaction medium. As this poor solvent, for example Methyl alcohol, ethyl alcohol, Isopropyl alcohol, a cyclohexanol, ethylene glycol, Propylene glycol, 1,4-butanediol, triethylene glycol, An acetone, a methyl ethyl ketone, methyl isobutyl ketone, a cyclohexanone, Methyl acetate, ethyl acetate, butyl acetate, oxalic acid diethyl, a diethyl malonate, Diethylether, methyl cellosolve, ethylcellosolve, the ethylene glycol-n-propyl ether, The ethylene glycol-i-propyl ether, butyl cellosolve, ethylene glycol wood ether, Ethylene glycol ethyl ether acetate, diethylene-glycol wood ether, A tetrahydrofuran, dichloromethane, 1,2-dichloroethane, 1, 4-dichlorobutane, trichloroethane, chlorobenzene, o-dichlorobenzene, a hexane, a heptane, an octane, benzene, toluene, a xylene, etc. can be mentioned.

[0016] The liquid crystal orientation agent of this invention contains the mixed solvent (B) which contains gamma-butyrolactone and a N-methyl-2-pyrrolidone, and has preferably 0.1 - 50 % of the weight of content of a N-methyl-2-pyrrolidone in 1 - 40% of the weight of the range. If the variation in thickness exceeds [the content of a N-methyl-2-pyrrolidone] **50- at less than 0.1 % of the weight and

the content of a N-methyl-2-pyrrolidone exceeds 50 % of the weight, the thickness nonuniformity by film milkiness will become large conversely.

[0017] The mixed solvent (B) in this invention can contain other solvents other than gamma-butyrolactone and a N-methyl-2-pyrrolidone if needed, this -- others -- as for the content of a solvent, it is desirable to carry out to about 80 or less % of the weight of the whole mixed solvent (B).

[0018] This -- others -- as a solvent, alcohols of the phenol system solvent; above-mentioned, such as aprotic system polar-solvent; m-cresol, such as N,N-dimethylacetamide, N,N-dimethylformamide, dimethyl sulfoxide, tetramethylurea, and hexamethylphosphoramide, a xylenol, a phenol, and a halogenation phenol, ketones, ester, ether, halogenated hydrocarbon, and hydrocarbons can be mentioned, for example.

[0019] Moreover, the liquid crystal orientation agent of this invention is the purpose which improves the adhesive property of polyamic acid and/or fusibility polyimide, and a substrate, and can contain a functionality silane content compound.

[0020] As a functionality silane content compound, for example 3-aminopropyl trimethoxysilane, 3-aminopropyl triethoxysilane, 2-aminopropyl trimethoxysilane, 2-aminopropyl triethoxysilane, N-(2-aminoethyl)-3-aminopropyl trimethoxysilane, N-(2-aminoethyl)-3-aminopropyl methyl dimethoxysilane, 3-ureido propyltrimethoxysilane, 3-ureido propyl triethoxysilane, N-ethoxycarbonyl-3-aminopropyl trimethoxysilane, N-ethoxycarbonyl-3-aminopropyl triethoxysilane, N-triethoxy silyl propyl TORIECHIREN triamine, N-trimethoxysilylpropyl TORIECHIREN triamine, 7-thoria ZADEKAN 10-TORIME -- an ibis -- C silyl - 1, 4, 7-thoria ZADEKAN, and 10-triethoxy silyl - 1 and 4 -- 9-trimethoxysilyl - 3, 6-diaza nonyl acetate, 9-triethoxy silyl - 3, 6-diaza nonyl acetate, N-benzyl-3-aminopropyl trimethoxysilane, N-benzyl-3-aminopropyl triethoxysilane, N-phenyl-3-aminopropyl trimethoxysilane, N-phenyl-3-aminopropyl triethoxysilane, N-bis(oxyethylene)-3-aminopropyl trimethoxysilane, N-bis(oxyethylene)-3-aminopropyl triethoxysilane, etc. are mentioned.

[0021] The liquid crystal display component obtained using the liquid crystal orientation agent of this invention can be manufactured by the following approach. First, the liquid crystal orientation agent of this invention is applied by printing, it heats at the temperature of 120-200 degrees C more preferably, and 80-200 degrees C of paint films are made to form in the transporence electric conduction film side of the substrate with which the transporence electric conduction film was prepared preferably. 0.001-1 micrometer of this paint film is usually 0.005-0.5 micrometers preferably.

[0022] Let the paint film formed as mentioned above be the liquid crystal orientation film by performing rubbing processing with the roll which twisted the cloth which consists of synthetic fibers, such as nylon. As the above-mentioned substrate, the transporence substrate which consists of plastic film, such as glass, such as a float glass and soda glass, polyethylene terephthalate, polybutylene terephthalate, polyether sulphone, and a polycarbonate, etc., for example can be used.

[0023] As the above-mentioned transporence electric conduction film, the NESA film which consists of SnO₂, the ITO film which consists of In₂O₃-SnO₂ can be used, and the photo etching method, the approach using a mask, etc. are beforehand used for patterning of these transporence electric conduction film. In order to make still better the adhesive property of a substrate and the transporence electric conduction film, and a paint film on the occasion of spreading of a liquid crystal orientation agent, a functionality silane content compound, titanate, etc. can also be beforehand applied on a substrate and the transporence electric conduction film.

[0024] In the liquid crystal orientation film, it is filled up with liquid crystal, and a restoration hole is closed, consider [it is made to counter so that it may become conversely parallel, and the seal of the periphery between substrates be carried out by the sealing compound and] as a liquid crystal cell, and, as for the substrate with which the liquid crystal orientation film was formed, let [sheets / the / two] the direction of rubbing be a liquid crystal display component a rectangular cross or by making it rival so that the direction of rubbing of the liquid crystal orientation film of a substrate and the polarization direction are in agreement or may cross at right angles to the both sides, respectively.

[0025] As the above-mentioned sealing compound, the epoxy resin which contained the curing agent and the aluminum-oxide ball as a spacer, for example can be used. As the above-mentioned liquid

crystal, pneumatic mold liquid crystal, smectic mold liquid crystal, and the thing in which pneumatic mold liquid crystal is made to form also in it are desirable, for example, the Schiff base system liquid crystal, azoxy series liquid crystal, biphenyl liquid crystal, phenylcyclohexane system liquid crystal, ester system liquid crystal, terphenyl liquid crystal, biphenyl cyclohexane liquid crystal, pyrimidine liquid crystal, dioxane system liquid crystal, bicyclo octane system liquid crystal, cubane system liquid crystal, etc. are used. Moreover, cholesteric liquid crystal, such as cholesteryl chloride, KORESUTERIRUNONAETO, and cholesteryl carbonate, a trade name C-15, a chiral agent that is sold as CB-15 (Merck Ltd.) can also be added and used for such liquid crystal. Furthermore, ferroelectric liquid crystals, such as p-DESHIROKISHI benzyldiene-p-amino-2-methylbutyl cinnamate, can also be used.

[0026] As a polarizing plate used for the outside of a liquid crystal cell, the polarizing plate which sandwiched the polarization film called H film which made iodine absorb by the cellulose acetate protective coat, or the polarizing plate which consists of the H film itself can be mentioned, carrying out the stretch orientation of the polyvinyl alcohol.

[0027]

[Example] Hereafter, although an example explains this invention still more concretely, this invention is not restricted to these examples. In addition, the thickness of the liquid crystal orientation film was measured using the thickness gage (alpha step) of a sensing-pin type, and evaluated the thickness and its variation in respect of liquid crystal orientation film spreading.

[0028] The synthetic examples 12 and 3, 44.8g of 5-TORIKARUBOKI gardenia fruit clo pentyl acetic-acid 2 anhydrides, and 21.6g of p-phenylene diamines were dissolved in gamma-butyrolactone / N-methyl-2-pyrrolidone =50/50 (weight ratio) 988g, and it was made to react at a room temperature for 6 hours. Subsequently, the methanol of an overlarge was filled with the reaction mixture, and the resultant was settled. Then, the methanol washed, it was made to dry at 40 degrees C under reduced pressure for 15 hours, and polyamic acid Ia60.2g of intrinsic-viscosity 1.44 dl/g was obtained.

[0029] Polyamic acid Ia30.0g obtained in the example 1 of synthetic example 2 composition was dissolved in 570g gamma-butyrolactone, the 21.6g pyridine and the 16.74g acetic anhydride were added, and the imide-ized reaction reaction was carried out at 120 degrees C for 3 hours. Subsequently, reaction generation liquid was settled like the synthetic example 1, and polyimide IIa24.0g of intrinsic-viscosity 1.35 dl/g was obtained.

[0030] In the example 1 of synthetic example 3 composition, except having set diamine to 4 and 4'-diamino diphenylmethane 39.6g, polyamic acid Ib was obtained like the synthetic example 1, the imide-ized reaction was further performed like the synthetic example 2 using this polyamic acid Ib, and polyimide IIb22.2g of intrinsic-viscosity 1.16 dl/g was obtained.

[0031] In the example 1 of synthetic example 4 composition, intrinsic-viscosity 1.26 dl/g polyamic acid Ic50.5g was obtained like the synthetic example 1 except having made tetracarboxylic dianhydride into 39.22g of cyclobutane tetracarboxylic dianhydride.

[0032] In the example 1 of synthetic example 5 composition Polyamic acid Id is obtained like the synthetic example 1 except having set tetracarboxylic dianhydride to 1, 3,a [3], 4, 5, 9b-hexahydro-5-(tetrahydro - 2, 5-dioxo-3-furanyl)-[1 and 2-naphth c] furan -1, and 3-dione 60.0g. Furthermore, the imide-ized reaction was performed like the synthetic example 2 using this polyamic acid Id, and polyimide IId22.2g of intrinsic-viscosity 1.16 dl/g was obtained.

[0033] In the example 1 of synthetic example 6 composition, intrinsic-viscosity 1.66 dl/g polyamic acid Ie60.5g was obtained like the synthetic example 1 except having used tetracarboxylic dianhydride as 43.6g of pyromellitic acid 2 anhydrides.

[0034] The polymer Ia obtained in the example 1 of example 1 composition was dissolved in gamma-butyrolactone/N-methyl-2-pyrrolidone (= 95/5, a weight ratio), it considered as the solution of 5 % of the weight of solid content concentration, this solution was filtered with the filter of 1 micrometer of apertures, and the liquid crystal orientation agent solution was prepared. This solution was applied in the transparent electrode side on the glass substrate with a transparent electrode which consists of ITO film using the printing machine for liquid crystal orientation film spreading, and it dried at 180 degrees C for

